(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 April 2001 (12.04.2001)

PCT

(10) International Publication Number
WO 01/25496 A1

(51) International Patent Classification[7]: C22B 5/10, C10L 5/10, C01B 33/025

(21) International Application Number: PCT/NO00/00315

(22) International Filing Date: 27 September 2000 (27.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
19994783 1 October 1999 (01.10.1999) NO

(71) Applicant *(for all designated States except US)*: **ELKEM ASA** [NO/NO]; Hoffsveien 65B, N-0377 Oslo (NO).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **RAANESS, Ola** [NO/NO]; Dr. Sandsvei 13, N-7017 Trondheim (NO). **TVEIT, Halvard** [NO/NO]; Sandgata 20, N-7012 Trondheim (NO). **AUGANÆS, Egil** [NO/NO]; Vavoll 40, N-5610 Øystese (NO). **EIKELAND, Inger, Johaune** [NO/NO]; Sagadammen 26, N-0884 Oslo (NO).

(74) Agent: **VINDENES, Magne**; Elkem ASA Patentavd., P.O. Box 8040, Vågsbygd, N-4675 Kristiansand (NO).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/25496 A1

(54) Title: CARBON-CONTAINING AGGLOMERATES

(57) Abstract: The present invention relates to carbon containing agglomerates for use as a reduction material in production of metals and alloys. The agglomerates comprise a binder and 10 to 80% by weight of one or more fine particulate carbon materials dispersed in a carbon-containing material which has or which forms pores during heating.

Title of invention: Carbon-containing agglomerates.

Technical Field

The present invention relates to carbon-containing agglomerates for the use as reduction material in electric smelting furnaces for the production of metals and alloys, more particularly for the use in electric smelting furnaces for the production of pig iron, ferro alloys and silicon.

Background Art

In the production of pig iron, ferro alloys and silicon, fossile carbon in the form of lumpy coal or coke or biocarbon in the form of lumpy char coal and in the form of wood chips are used as reduction materials. It is further known to use agglomerates in the form of briquettes or pellets of pulverized coal or coke, optionally with addition of iron oxide or other metal oxides.

In many of these processes the reduction materials react with a gas phase, that is, carbon in the form of coke, coal or charcoal reacts with an oxidizing gas such as oxygen, carbonmonoxide or silicon monoxide. Lumpy carbon materials are in these processes consumed from the outside and releases continuously new unreacted surface.

In some instances the carbon containing reduction materials have to be crushed into a fine particulate material whereafter the fine particulate carbon materials are subjected to cleaning processes to achieve a desired purity. Mineral impurities can for instance be removed from coal by crushing the coal and separation of minerals from the coal by flotation. In other cases the carbon-containing material exists in fine particular forms, such as for instance carbon black. Further, there are available large amounts of fine particulate coal, coke and char coal as it is usual to remove these fines from the lumpy materials by sieving before the lumping material are used as reduction materials. Fines of coal and coke thus represent both an economic loss and a storage problem for producers of metals and alloys. Fine particulate reduction materials are normally not suited for supply to reactors and smelting furnaces

where they are to react with a gas. Typical problems that occur when fine particular reduction materials are added in such processes are that the charge in the reactor becomes too dense, thus not allowing the gas to pass through the reactor charge. Further, a part of the fine particulate reduction material is lost from the reactor with the off-gases.

In order to avoid these problems it is known to agglomerate fine particulate reduction materials before they are added to the reactor or to the smelting furnace. This is usually done by agglomerating the fine particulate reduction material by adding a suitable binder. It has, however, been found that such agglomerates have a low reactivity and are thus not well suited as reduction material for the production of pig iron, ferro alloys and silicon. It is assumed that the reason for the low reactivity for such agglomerates is that the agglomerators are to dense whereby the reaction gas will diffuse too slowly into the agglomerates.

In the production of silicon and ferrosilicon it is often a wish to obtain products with high purity. Most of the impurities are supplied to the silicon or the ferrosilicon through the reduction materials, while the silicon source, which normally is quartz, can be obtained at a high purity. In the production of silicon and ferrosilicon SiO-gas is formed as an intermediate compound when quartz is being reduced. More than 80 % of the energy supplied in the production of silicon and ferrosilicon is used to produce SiO-gas. It is therefore of vital importance that this chemical compound is conserved in the process. This is done by supply of carbon that forms or has a porous structure into which the SiO-gas can diffuse and react. The chemical reaction that occurs is:

$$SiO(gas) + 2C(solid) = SiC(solid) + 2CO(gas).$$

Examples of pure carbon containing reduction materials are petrol coke and carbon black. These materials do, however, have properties which make them unsuitable as reduction materials due to the fact that they are not able to react quickly with the SiO gas and thus conserve this in the process.

Particularly, for production of silicon it is a wish to be able to use petrol coke and carbon black as reduction materials as these carbon materials have a very low content of impurities and thus can be used for production of high purity silicon.

With fine particulate carbon materials it shall herein be understood carbon materials where a substantial part passes through a sieve with square light openings of 3 mm.

Disclosure of Invention

By the present invention one has now arrived at an agglomerate which contains a substantial amount of fine particulate carbon materials which agglomerates show a surprisingly high reactivity when used as a reduction material in metallurgical metal reduction processes and which have a sufficient mechanical strength to withstand transport to smelting furnaces.

The present invention thus relates to carbon containing agglomerates for use as a reduction material in production of metals and alloys, which agglomerates are characterized in that they comprise a binder and 10 to 80 % by weight of one or more fine particulate carbon materials dispersed in a carbon-containing material which has or which forms pores during heating.

According to a preferred embodiment the agglomerates contain one or more fine particulate carbon materials selected among the group of petrol coke, char coal, carbon black and coal.

The agglomerates preferably comprise between 25 and 70 % by weight of fine particulate carbon material.

The carbon-containing material which has or forms pores during heating is preferably a baking coal with a free swelling index of more than 4, pitch, tar or biomass. The free swelling index for coal varies between 0 and 10 according to the ASTM standard.

As biomass it can be used a biomass having a fibre length which is adjusted to the size of the agglomerates and which preferably are pretreated by cutting or crushing or which is in the form of a waste material having a suitable fibre length, such as sawdust. Biomass treated with water vapour under high pressure has been found to be particularly suited as a porous carbon-containing material for dispersion of the fine particulate carbon materials.

As a binder it can be used binders or combinations of binders which give sufficient strength to the agglomerates at low temperatures in order to transport the agglomerates without producing to much fines and which gives the agglomerates sufficient strength at high temperature to avoid desintegration when the agglomerates are supplied to a smelting furnace.

It can be used combinations of binders to ensure that the agglomerates have a sufficient strength both at low and at high temperatures.

As binders it can be used thermosetting resins, lignin or similar binders which give a good strength at low temperatures and which forms a binder phase of carbon when heated to provide a good strength at high temperatures.

Other binders that can be used are carboxy methyl cellulose (CMC) which gives a good strength at low temperatures, but has a low coke value that gives a relative low strength at high temperature. CMC is therefore preferably combined with other binders that give the agglomerates an increased strength at high temperatures. Examples of such binders are baking coals, tar, pitch and bituminous compounds obtained from distillation of oil. Baking coal, tar and pitch can thus be used both as carbon-containing porous material for dispersion of the fine particulate carbon materials and as a binder in the agglomerates.

Other binders that can be used are water glass or starch together with a high temperature binder such as baking coal, tar, pitch or bituminous compounds from distillation of oil.

It has surprisingly been found that the agglomerates according to the present invention have a very high reactivity. While lumpy petrol coke shows a very low SiO reactivity, agglomerates according to the invention where the carbon material is fine particulate petrol coke dispersed in a carbon-containing material that has or forms pores during heating, have a SiO reactivity which is at least as good as the best available lumpy carbon reduction material.

It is believed that the main reason for the very high SiO reactivity for the agglomerates according to the invention is due to the fact that the fine particulate carbon particles are dispersed in the carbon-containing material that has or forms pores during heating, whereby a very high surface area is available for the reaction gases.

Detailed description of the Invention

The present invention will now be further described by way of examples.

EXAMPLE 1 (Prior Art)

A reaction chamber was filled with lumpy petrol coke having a particle size between 4 and 6.35 mm and the SiO reactivity for the petrol coke was measured.

SiO reactivity was measured by means of a standardized method where a gas mixture consisting of 13.5 % SiO, 4.5 % CO the remainder being argon, at a temperature of about 1650°C is passed through a bed of the material to be tested. When the gas mixture comes into contact with the carbon material in the bed, more or less SiO(g) will react with the carbon to form SiC and CO-gas. The content of CO in the gas mixture which has passed through the carbon materials in the bed is analyzed and the amount of SiO which has reacted with carbon for the formation of SiC is calculated. The amount of SiO which passes the bed unreacted gives a measure for the reactivity as a low amount of SiO reflects a high reactivity while a high amount of SiO reflects a low reactivity. This method is described in the paper "Reactivity of reduction materials in the production of Silicon, Silicon-rich Ferro alloys and Silicon-

Carbide" by J.Kr. Tuset and O. Raaness, AIME El. Furnace Conference, St.Lois, Miss, Dec. 1979.

When the off-gas analysis showed that all carbon in the petrol coke was reacted to silicon carbide, 4700 ml of SiO gas had reacted with the carbon to silicon carbide, while 3500 ml SiO gas had passed through the reactor without reacting.

EXAMPLE 2

It was produced an agglomerate according to the invention consisting of 67 % fine particulate petrol coke and 33 % biomass and with lignin as a binder. The agglomerate had a particle size between 4 and 6.35 mm. The agglomerates were filled into the reactor in the same amount as in example 1 and the SiO reactivity was measured. When the off-gas analysis showed that all carbon in the agglomerates was reacted to silicon carbide, 4700 ml SiO had reacted with the carbon to form silicon carbide while 500 ml SiO gas had passed through the reactor without reducing.

By comparing the amount of unreacted SiO in examples 1 and 2 it will be seen that the agglomerates according to the present invention containing fine particulate petrol coke show a surprisingly increased SiO reactivity compared to the SiO reactivity of lumpy petrol coke according to example 1.

EXAMPLE 3 (Prior Art)

Char coal produced from eucalyptus tree was crushed and placed in the reaction chamber mentioned in example 1. The SiO reactivity was measured in the same way as described in example 1. When all carbon in the char coal had reacted to silicon carbide, 2700 ml SiO gas had reacted with the carbon to silicon carbide, while 600 ml SiO passed through the reactor without reacting.

EXAMPLE 4

It was produced agglomerates according to the present invention by mixing 40 % by weight fines from char coal and 60 % by weight biomass and adding lignin as a binder. The agglomerates were supplied to the reactor in such an amount that the amount of carbon in the reactor was the same as in example 3. The SiO reactivity was thereafter measured. When all carbon in the agglomerates had reacted to silicon carbide, 2700 ml SiO gas had reacted with the carbon to silicon carbide while 280 ml SiO gas had passed through the reactor without reacting. By comparing the results from example 3 and 4 it can be seen that the SiO reactivity of the agglomerates according to the invention was substantially higher than the SiO reactivity for char coal, even though lumpy char coal is considered as the carbon reduction material having the highest SiO reactivity.

EXAMPLE 5 (Prior Art)

Lumpy coal was heated in inert atmosphere at 1200°C for formation of coke. The produced coke was placed in the reaction chamber in the same way as described in example 1.

The SiO reactivity was measured in the same way as in example 1. When all carbon in the coke has reacted to silicon carbide, 5600 ml SiO gas had reacted with the carbon to form silicon carbide while 800 ml SiO gas had passed through the reactor without reacting.

EXAMPLE 6

It was produced agglomerates according to the invention by mixing 40 % by weight of fines from the coal used in example 5 with 60 % by weight of biomass and with lignin as binder. The agglomerates were supplied to the reactor in an amount providing the same amount of carbon as in example 5, whereafter the SiO reactivity was measured. When all carbon in the agglomerates had reacted to silicon carbide, 5600 ml SiO had reacted with

the carbon to silicon carbide, while 400 ml SiO gas had passed through the reactor without reacting.

By comparing the results from example 5 and 6 it can be seen that the SiO reactivity of the agglomerates according to the present invention containing fine particulate coal was appreciably higher than the SiO reactivity of coke produced from the same type of coal.

EXAMPLE 7

It was produced agglomerates according to the present invention consisting of 50 % fine particulate petrol coke and 50 % Longyear coal from Spitsbergen having a free swelling index between 8 and 9 and a particle size of less than 1 mm. 3 % by weight of water glass was added as a binder. The mixture was agglomerated and heated to 1200°C in an inert atmosphere. The agglomerates were supplied to the reactor in the same amount as in example 1 and the SiO reactivity was measured. When the off-gas analysis showed that all carbon in the agglomerates had reacted to silicon carbide, 1200 ml SiO gas has passed the reactor without reacting. By comparing with example 1 this example shows that the reactivity of petrol coke increases substantially by using baking coal as a porous forming medium for petrol coke.

CLAIMS

1. Carbon containing agglomerates for use as a reduction material in production of metals and alloys, characterized in that they comprise a binder and 10 to 80 % by weight of one or more fine particulate carbon materials dispersed in a carbon-containing material which has or which forms pores during heating.

2. Carbon-containing agglomerates according to claim 1, characterized in that the fine particulate carbon materials are selected among the group of petrol coke, char coal, carbon black and coal.

3. Carbon-containing agglomerates according to claim 1, characterized in that they comprise between 25 and 70 % by weight of fine particulate carbon material.

4. Carbon-containing agglomerates according to claim 1, characterized in that the carbon-containing material which has or forms pores during heating is selected among a baking coal with a free swelling index of more than 4, pitch, tar and biomass.

5. Carbon-containing agglomerates according to claim 1, characterized in that they contain biomass treated with water under high pressure.

6. Carbon-containing agglomerates according to claim 1, characterized in that the binder is lignin.

7. Carbon-containing agglomerates according to claim 1, characterized in that the binder is a thermosetting resin.

8. Carbon-containing agglomerates according to claim 1, characterized in that the binder is carboxy methyl cellulose.

9. Carbon-containing agglomerates according to claim 1, characterized in that the binder is a mixture of carboxy methyl cellulose and a high temperature binder selected among baking coal, tar, pitch and bituminous compounds from the distillation of ribs.

10. Carbon-containing agglomerates according to claim 1, characterized in that the binder is a mixture of water glass and a high temperature binder selected among baking coal, tar, pitch and bituminous compounds from the distillation of oils.

11. Carbon-containing agglomerates according to claim 1, characterized in that the binder is a mixture of starch and a high temperature binder selected among baking coal, tar, pitch and bituminous compounds from the distillation of oils.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 00/00315

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C22B 5/10, C10L 5/10, C01B 33/025

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C22B, C10L, C01B, C21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1089572 A (WU W) 1994-07-20 (abstract) World Patents Index (online). London, U.K.:Derwent Publications, Ltd. (retrieved on 2001-01-08). Retrieved from: EPO WPI Database. DW199534, Accession No. 1995-255521 --	1-11
X	DE 3227395 C2 (GEWERKSCHAFT SOPHIA-JACOBS STAINKOHLENBERGWERK), 23 May 1991 (23.05.91) --	1-4,6-11
A	US 5002733 A (ERNEST J. BRETON ET AL), 26 March 1991 (26.03.91), column 2, line 20 - line 24 --	1-11

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 January 2001	15-01-2001

Name and mailing address of the ISA/	Authorized officer
Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Bertil Dahl/ELY Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 00/00315

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 3320660 A1 (SIEMENS AG), 13 December 1984 (13.12.84), page 3, line 13 - line 16 --	1-11
A	JP 61034096 A (OSAKA GAS CO LTD) 1986-02-18 (abstract) World Patents Index(online).London, U.K.: Derwent Publications, Ltd. (retrieved on 2001-01-08) Retrieved from: EPO WPI Database. DW198613, Accession No. 1986-085962 --	1-11
A	SU 901314 B (MOSCOW STEEL ALLOYS INST et al) 1982-01-30 (abstract) World Patents Index (online). London, U.K.: Derwent Publications, Ltd. (retrieved on 2001-01-08). Retrieved from: EPO WPI Database. DW198248, Accession No. 1982-04099J -- --------	1-11

INTERNATIONAL SEARCH REPORT
Information on patent family members

04/12/00

International application No.
PCT/NO 00/00315

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3227395 C2	23/05/91	NONE	
US 5002733 A	26/03/91	NONE	
DE 3320660 A1	13/12/84	NONE	